SIMULATION OF HETEROGENEOUSLY CATALYSED ESTERIFICATION FOR THE BIODIESEL PRODUCTION USING REACTIVE DISTILLATION COLUMN

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STUDENT DECLARATION

I declare that this plant design project entitled "*Simulation of Heterogeneously Catalysed Esterification for the Biodiesel Production using Reactive Distillation Column*" is the result of my own research except as cited in the references. The project has not been accepted for my any degree and is not concurrently summated in candidature of any other degree.

Signature	:	……..
Name of Student	:	Kelvin Chong Chee An
Date	:	……..

To my beloved mother and father

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ABSTRACT

Biodiesel has become an attractive focus due to its environmental friendliness and benefits. Waste and non-edible raw materials have been employed for producing biodiesel in order to make it competitiveness with the petroleum-based diesel. Waste raw materials can contain substantial amount of free fatty acids (FFAs). Esterification reaction is one of the major routes to produce biodiesel from the raw material with high FFAs. However, the conventional process is facing several problems. Therefore, the development of an efficient continuous process for biodiesel manufacturing is required in which the use of a solid catalyst is highly desirable in order to suppress costly chemical processing steps and waste treatment. In the present study, an innovative esterification process of fatty acids based on reactive distillation was proposed for the biodiesel production. Process simulation was performed to study the feasibility of producing biodiesel using reactive distillation column, to identify the important operating and design factors (reactant ratio, reflux ratio, pressure, distillate-to-feed ratio, number of stages, and catalyst weight), and to propose a suitable configuration of the pilot plant for the biodiesel production. The esterification process was modelled by the esterification of oleic acid with methanol. The reaction was catalysed heterogeneously by sulfonic exchange acid resin. A pragmatic kinetic based on pseudohomogeneous model was incorporated into the reactive distillation model. From the simulation, it was found that it is feasible to produce biodiesel using reactive distillation column. The distillate-to-feed is best suited at 0.4 while the reflux ratio is best-suited in the range of 0.04 to 0.10. Pressure can be up to 3 bar. The changes in catalyst weight apparently contribute to the scale of production for biodiesel. The catalyst weight used is in the range of 250 to 500 gm. Finally, a suitable reactive distillation column configuration was proposed.

ABSTRAK

Biodisel telah menjadi satu tarikan kerana ia bersifat semulajadi and mempunyai pelbagai kebaikan. Sisa buangan and bahan mentah yang tidak boleh dimakan boleh digunakan untuk menghasilkan biodiesel supaya dapat bersaing dengan diesel daripada petroleum. Sisa buangan mentah mengandungi kandungan asid lemak yang tetap. Esterifikasi merupakan salah satu cara untuk menghasilkan biodiesel daripada sisa buangan mentah yang mengandungi asid lemak yang tinggi. Walau bagaimanapun, proses konveksional mengalami beberapa masalah teknikal. Sedemikian, penciptaan proses gabungan yang lebih efisien untuk biodiesel produksi yang memerlukan penggunaan pemangkin heterogen kerana permintaan yang tinggi justeru merendahkan kos langkah pemprosesan kimia dan kos rawatan bahan buangan. Kajian masa kini, satu inovasi dalam proses esterifikasi asid lemak telah melibatkan penyulingan bertindak balas dicadangkan untuk menghasilkan biodiesel. Proses simulasi telah dijalankan untuk mengkaji kebolehan menggunakan "reactive distillation" untuk menghasilkan biodiesel, menentukan kepentingan operasi dan faktor rekabentuk (nisbah bahan tindak balas, nisbah refluk, tekanan, nisbah bahan tersuling kepada suapan, bilangan peringkat dan berat pemangkin), dan mencadangkan konfigurasi yang sesuai untuk pembinaan logi berpandu bagi menghasilkan biodiesel. Proses esterifikasi dimodelkan sebagai esterifikasi asid oleik dengan metanol. Tindak balas dimangkin dengan menggunakan pemangkin heterogen "sulfonic exchange acid resin". Satu pragmatik kinetik yang menggunakan "pseudohomogeneous" model digabungkan dengan model penyulingan bertindak balas. Daripada simulasi, keputusan yang diperolehi menunjukkan biodiesel dapat diproduksi dengan menggunakan "reactive distillation" ruangan. Nilai yang sesuai untuk nisbah bahan tersuling kepada suapan ialah 0.4 manakala nisbah refluk boleh menggunakan nilai antara 0.04 hingga 0.10. Tekanan boleh dinaikkan sehingga 3 bar. Perubahan dalam berat pemangkin didapati memberi kesan kepada perubahan dalam

penghasilan biodiesel. Berat pemangkin yang digunakan adalah antara 250 hingga 500 gm. Akhirnya, satu konfigurasi yang sesuai untuk penghasilan biodisel melalui penyulingan bertindak balas telah dicadangkan.

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SYMBOL	DEFINITION
a	liquid activity
A	pre-exponential factor in Arrhenius equation, units according to k
C	molar concentration in liquid phase, mol m^{-3}
C_{cat}	catalyst hold-up per unit of liquid phase volume, kg m^{-3}
C_{ref}	reference concentration for Damköhler number, mol m^{-3}
Da_1	Damköhler number for non-catalysed reaction
Da_2	modified Damköhler number for catalysed reaction
E_a	activation energy, kJ mol^{-1}
F_{acid}	molar flow rate of oleic acid, kmol h^{-1}
G_V	volumetric flowrate, m^3 s^{-1}
k_c	rate constant for the catalysed reaction, m^6 s^{-1} mol^{-1} kg^{-1}
k_{ref}	rate constant for the non-catalysed reaction, m^6 s^{-1} mol^{-1} kg^{-1}
K_a	concentration-based reaction equilibrium constant
K_γ	ratio of liquid activity coefficients
K_x	activity-based reaction equilibrium constant
n	molar feed ratio of methanol : oleic acid
n_1, n_2	reaction orders for non-catalysed reaction
P	pressure, Pa
r	reaction rate per unit of liquid volume, mol s^{-1} m^{-3}
R	gas constant, J mol^{-1} K^{-1}
V	total liquid hold-up in the RD column, m^3
V_M	liquid molar volume, m^3 mol^{-1}

T	temperature, K
W_{cat}	catalyst hold-up in RD column, kg

Subscripts

acid	oleic acid
alcohol	methanol
cat	sulfonic exchange acid resin
ester	methyl oleate
0	initial or at zero conversion
ref	reference variable

Superscripts

*	modified, by including liquid activity coefficients
eq	at chemical equilibrium
liq	in liquid phase

Greek letters

$\Delta^r G_{P,T}^{liq}$	Gibbs free energy of reaction at P and T, kJ mol^{-1}
φ_1	ratio of non-catalysed to catalysed reaction rate
φ_2	ratio of the product of liquid activities to K_a
γ	liquid activity coefficient

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Biodiesel has become attractively focus and important because of the fast-paced depleting of petroleum reserves and also of its environmental friendliness and benefits. Biodiesel is an alternative fuel produced from renewable source (Berchmans *et al*., 2007; Santacesaria *et al*., 2007) which has low emission profile property minimising carbon dioxide emission. Thus, this fuel can be regarded as mineral diesel substitute with the benefit of lowering greenhouse emissions because it is a renewable resource (Felizardo *et al*., 2006). However, the high cost of biodiesel is the major obstacle for its commercialisation; the biodiesel produced from vegetable oil or animal fat is usually more expensive than petroleum-based diesel fuel from 10 to 50% (Leung *et al*., 2006). Alternatively, the production costs can be reduced using less expensive feedstocks containing fatty acids such as non-edible oils, animal fats and oils, fritter away oil and byproducts of the refining vegetables oils (Veljkovic´ *et al*., 2006). Biodiesel has many environmental beneficial properties. Biodiesel can be described as 'carbon neutral' which means the fuel produces no net output of carbon in the form of carbon dioxide (CO_2). Studies shows that the effect is caused by the oil crop absorbed the same amount of CO_2 when it grows and releases when the fuel is combusted. However, the amount of carbon dioxide cannot be properly associated as there are contributors to the green house gases such as the

production of the fertiliser. Biodiesel is a rapid biodegradable and completely non-toxic, meaning spillages represent far less of a risk than fossil diesel spillages. Besides that, biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash.

Most biodiesel produced nowadays are from waste vegetable oil sourced from restaurant, chip shops, industrial food producers. Currently, the usage of oil directly from the agricultural industry has the greatest potential source being not commercially produced as the raw oil is too pricy. The cost of converting raw oil from agricultural sources can be too expensive to compete with fossil diesel. Therefore, waste vegetable oil can often be sourced for free or sourced already treated for a small price.

Biodiesel has many environmental beneficial properties. Biodiesel can be described as 'carbon neutral' which means the fuel produces no net output of carbon in the form of carbon dioxide (CO_2). Studies shows that the effect is caused by the oil crop absorbed the same amount of CO_2 when it grows and releases when the fuel is combusted. However, the amount of carbon dioxide cannot be properly associated as there are contributors to the green house gases such as the production of the fertiliser. Biodiesel is a rapid biodegradable and completely non-toxic, meaning spillages represent far less of a risk than fossil diesel spillages. Besides that, biodiesel has a higher flash point than fossil diesel and so is safer in the event of a crash.

There are five primary ways of producing biodiesel: (i) direct use and blending of vegetable oil (Maa *et al*., 1990), (ii) the usage of microemulsions with short-chain alcohols (Maa *et al.*, 1990), (iii) thermal cracking of vegetable oils (Charusiri *et al*., 2005), (iv) transesterification of triglycerides catalysed by acids, bases or enzymes, and (v) esterification of fatty acids with alcohols, using acids catalysts, solids acids (Kiss *et al*., 2006a, Kiss *et al*., 2006b) or bioenzymes (Foresti

et al., 2007). Using transesterification reaction, biodiesel production is normally catalysed by alkaline homogeneous catalyst to form a mixture of fatty acid methyl esters (Santacesaria *et al*., 2007). Alkaline catalyst could result soap formation if the feedstock used contains substantial amount of free fatty acids. The acid catalysed esterification reaction is one of the suitable routes to solve the problem.

Production of biodiesel is believed to be economical as it derives from biological sources such as vegetable oils or recycled cooking grease or oils. Biodiesel is an alternative source of energy produced by either esterification or transesterification process by converting oils or fats with appropriate alcohols. In orlder days, production of biodiesel uses separated reactor and distillation column which needs high capital costs. As technology advances, the combination of reaction and distillation within one unit operation called reactive distillation is widely used in industry for processes.

For scaling-up and optimizing the production of biodiesel, reactive distillation has a solid approach and compromise for the process. Besides that, the use of reactive distillation is a better choice as the combination of reaction and distillation offers a lower capital cost compared to the usage of a reactor and a distillation column.

1.2 Identification of Problems

Steinigeweg *et al*. (2003), Omota *et al*. (2003), Kiss *et al*. (2007;2008) and Matallana *et al*. (2000) have carried out experiments for the heterogeneously catalysed esterification for the production of biodiesel using reactive distillation

column. The outcome of these researchers is mostly in experimental works. Therefore, a simulation must be run to ensure the validity of data.

A simulation must be carried out to predict the results and study the possibilities before a plant can be built for production purposes. Simulation also useful for the preliminary design before a pilot plant is being built for experiment study. In the present study, the performance of the esterification of oleic acid and methanol catalysed by sulfonic exchange acid resin in the reactive distillation will be simulated by incorporating the thermodynamics model, kinetic model, and the reactor model.

Aspen-Plus simulator will be used as a tool for the simulation by incorporating the appropriate thermodynamics and kinetic models. The influence of important operating and design factors (reactant ratio, reflux ratio, pressure, distillate-to-feed ratio, size of the reactive section and catalyst weight) will be identified.

1.3 Objectives

The objectives of the studies are:

1. To study the feasibility of producing biodiesel using reactive distillation column.
2. To identify the important operating and design factors for the reactive distillation process.
3. To propose a suitable configuration of the pilot plant for the biodiesel production.

1.4 Scope of Study

In order to achieve the objectives of this project, the scopes of study are as below:

1. The thermodynamics model, kinetic model and reactive distillation model of the selected chemical biodiesel equation, i.e. esterification of oleic acid and methanol using sulfonic exchange acid resin will be analysed and screened.
2. Using Aspen-Plus version 12.1, the models are inserted to run simulation. Results obtained are to verify the feasibility of reactive distillation for production in real industry.
3. The important operating parameters such as reactant ratio, reflux ratio, pressure, distillate-to-feed ratio, number of stages and catalyst weight will be studied.

1.5 Rationale and Significance

Rationale. The objective of the present study is to simulate a heterogeneously catalysed esterification for the production of biodiesel using reactive distillation. Laboratory experiments have proven the reactivity of oleic acid and methanol using sulfonic exchange acid resin as catalyst to produce biodiesel. In this research, the results obtained from simulation for the feasibility studies on reactive distillation column can be used to replicate into dynamic business reality.

Significance. Simulation is one of many engineering design method used to study feasibility of a process. From the studies on the feasibility of reactive distillation column, the results can be used to setup an optimised reactive distillation

pilot plant. The pilot plant is built based on the suitable configuration results which then use to generate experiment data. The experiment data that generated from reactive distillation pilot plant is then used to build a production plant using reactive distillation for the production of biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Reactive distillation is a hybrid process that combines the reaction and separation in single equipment. The combination of reaction and separation into one single unit provides distinct advantages over the conventional, sequential approach. A reactive distillation includes a distillation column, flashers, strippers and condensers.

The combination (reactor and distillation) is advantageous as when the rate of chemical reaction is decreased by the reaction equilibrium resulting into poor yield, selectivity and conversion. The combination of separation process within the reactor induces better reaction products removal from the reaction zone thus improving the overall yield, selectivity and conversion compared to a conventional process.

Industrial reactive distillation systems comprise homogeneous and heterogeneous catalysed, irreversible and reversible reactions, covering large ranges of reactions, notably hydrogenations, hydrosulfurisation, esterifications, and etherification. The

system may contain multiple catalyst systems, gas and liquid internal recycle traffic over these catalyst systems, separation, mass flow, and enthalpy change.

2.2 General Esterification System

Esterification is a chemical reaction process involving two reactants typically an alcohol and an acid to form an ester as a product. Esters have characteristic pleasant and fruity odour. Esterification is a reversible reaction that therefore, the reactions are equilibrium reactions and need to be driven to completion according to Le Chatelier's principle.

1. Esterification of acetic acid with ethanol, catalysed both homogeneously by the acetic acid, and heterogeneously by Amerlyst-15 (Calvar *et al*., 2007).
2. Heterogeneously catalysed esterification of acetic acid with isoamyl alcohol with cation-exchanged resin catalyst, Purolite CT-175 (Teo *et al*., 2004).
3. Esterification of acetic acid with butanol in a heterogeneous reaction system using solid acid catalysts such as Smopex-101, Amberlyst-12, sulphated ZrO_2, H-USY-20, H-BETA-12.5, H-MOR-45, Nb_2O_5, H-ZSM-5-12.5 (Peters *et al*., 2006).

2.3 Biodiesel System

Biodiesel is the newest attraction to substitute the diesel fuel due to its environment benefits, but also for being a renewable and sustainable source of energy. Biodiesel is produced nowadays mainly by the transesterification of vegetable oils in the presence of basic homogeneous catalysts (NaOH, KOH, or related alkoxides), according to Santacesaria *et al*. (2007). Acids oils have become a new raw material for biodiesel production beside vegetable oils or animal fat but the amount of free fatty acid contains in acid oils exceed the maximum allows for conventional homogeneous basic technology. Because of this, heterogeneous catalyst can be used to perform the esterification reaction of the free fatty acid as well as transesterification of the triglycerides. Table 2.1 shows studies that have been done on biodiesel system via esterification process.

Table 2.1 : Biodiesel production via esterification.

Reactant System Used	Reference
Esterification of decanoic acid with methanol using strong acidic ion-exchange resin.	Sven Steinigeweg and Jurgen Gmerhling. (2003)
Esterification of palm fatty acids using homogeneous acid catalysts in a batch reactor.	Donato A.G. Aranda, Rafael T.P. Santos, Neyda C.O. Tapanes, Andre Luis Dantas Ramos, Octavio Auqusto C. Antunes (2007)
Esterification of free fatty acids using sulphuric acid as catalyst in the presence of triglycerides.	J. M. Marchetti, A.F. Errazu (2008)
Esterification of free fatty acids in sunflower oil over solid acid catalysts using batch and fixed bed-reactors	J. Ni, F.C. Meunier (2007)
Esterification of dodecanoic acid with methanol, propanol or 2-ethylhexanol using sulphated metal oxides (zirconia, titania, and tin oxide)	Anton A. Kiss, Alexandre C. Dimian and Gadi Rothenberg (2007)
The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel	Young-Moo Park, Dae-Won Lee, Deog-Keun Kim, Jin-Suck Lee, Kwan-Young Lee

2.4 Catalysis in Esterification

In general, catalysis can be divided into autocatalytic, homogeneous or heterogeneous and it is meticulously applicable to the reactive distillation column.

Autocatalysis only occurs when a single chemical reaction whose reaction product is itself the catalyst for the reaction. Autocatalysis reactions' reaction velocity is much compliance to be influenced by the reaction temperature, in other words, the pressure plays a proportion role to the effect of temperature of equipment.

Homogeneous catalysis on the other hand is likely to be influenced by the changing of concentration to enhance or lower the reaction velocity. Meanwhile, Heterogeneous catalysis requires a structure to pack the catalyst particles on the reaction zone in the RD column. Reaction catalysed by heterogeneous catalysts is very limited in the changes of its reaction velocity because it can only be enhanced to a certain concentration range and higher temperature or pressure will degrade the effectiveness of the catalyst as it contains ion-exchange particles, whose temperature range is limited.

2.4.1 Homogeneous

Fundamentally, homogeneous catalysis is a chemistry term describing the catalyst is in the same phase (solid, liquid or gas) as the reactants. The catalysts use in biodiesel production using homogeneous catalyst is less-preferred compare to

heterogeneous catalyst. The reactions proceed over an intermediate complex and are often highly selective, but separation of the products and the catalyst is difficult.

Homogeneous catalysts can be divided to two types:

a) Base catalysts: sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide (NaMeO);
b) Acid catalysts: sulphuric acid (H_2SO_4), p-toluene sulfonic acid (PTSA), MSA, phosphoric acid (H_3PO_4), calcium carbonate ($CaCO_3$);
c) Typical base concentrations are:
    a. NaOH/KOH – 0.3 to 1.5%
    b. NaMeO – 0.5% or less

The usage of homogeneous catalyst in biodiesel production will eventually constrain the developing of the yield as the catalyst is sensitive to free fatty acids (FFAs) and water content of the feedstock; the removal of catalyst after production; during the reaction, formation of soap with high FFA feedstock; large quantity of effluent water as a result of removal of catalyst; necessities pre-treatment of oil in case FFA content are higher; and no scope for regeneration or re-utilisation of the catalyst.

2.4.2 Heterogeneous

Heterogeneous catalysis is basically a catalyst in different phase (i.e. solid, liquid and gas, also oil and water) to the reactants. Heterogeneous catalysts provide a platform or surface for the chemical reaction to take place on. Separation of catalyst and products

is easy, but the reaction is often less selective, because the catalyst material is not homogeneous.

Heterogeneous catalysts are such as sulphated zeolites and clays, hetro-poly acids, metal oxides, sulphates, and composite materials. Contradict to homogeneous catalyst, heterogeneous catalyst is preferred and beneficial as the catalyst can be regenerated thus reduces the catalyst cost; utilization of lower quantity feed stocks for biodiesel production; simplification of separation process thus reduces capital cost; and as well decrease in wastewater which develops environmental friendly process.

2.5 Reactive Distillation Technology

2.5.1 Introduction

Reactive distillation (RD) is a combination of a reaction and separation in a single unit. It is not a new concept application which includes the functions of enhancement and overall performance in the chemical engineering world. Overall, the production of propylene oxide, ethylene dichloride, sodium methoxide, and various esters of carboxylic acids are some examples of processes in which RD found similarity in application and gains not much attractive attention.

Reactive distillation has proven to able in rendering cost-effectiveness and compactness to a chemical plant which the evidence from the Eastman Kodak process that compacted the whole chemical plant methyl acetate in a single RD unit. In this

chapter, the overview of an RD column will be discussed in its direction and suggestion on its potential. The objectives of using an RD are to: surpass equilibrium limitation, achieve high selectivity towards a desired product, achieve energy integration, perform difficult separations, and so on.

Table 2.2 gives a wide-ranging list of the reactions that have been investigated as candidates for RD.

Table 2.2 : Industrially important reactions using RD.

Reaction	Catalyst/Column internals etc.	Remarks on motives and achievements
Etherification		
methanol + isobutene = methyl *tert* butyl ether (MTBE)	Amberlyst 15	To enhance the conversion of isobutene and achieve separation if isobutene from C_4 stream
methanol + isoamylene = *tert* amyl methyl ether (TAME)	Ion-exchange resin	To enhance the conversion of isoamylene
Esterification with alcohols/olefins		
acetic acid + methanol = methyl acetate + water	Dowex 50 W X-8	Recovery of acetic acid from dilute streams (30 – 60% w/w)
	Amberlyst 15 (baskets on tray) Katamax packing	Recovery of acetic acid from dilute streams (2.5 – 10% w/w)
	Sulphuric acid	Recovery of dilute acetic acid in carbonylation process
		Manufacture of methyl acetate; overcomes azeotrope

		formation; enhances conversion (>99%)
Synthesis of vinyl acetate		
acetaldehyde + acetic anhydride = vinyl acetate		Improved safe process with high yields
Hydrolysis		
methyl acetate + water = methanol + acetic acid	Ion-exchange resin bags	Recovery of acetic acid and methanol in polyvinyl alcohol (PVA) and terephthalic acid (PTA) manufacture
	Fluidized RD	
	Cation exchanger on inert	Recovery of acetic acid in PVA manufacture
Acetalisation		
methanol + aqueous formaldehyde = methylal + water	Ion-exchange resins zeolites, ion-exchange resins	To surpass equilibrium conversion; to remove formaldehyde as an impurity (e.g., from 1,2-butyene diol)
ethanol + aqueous formaldehyde = ehtylal + water	Ion-exchange resins	Recovery of formaldehyde and synthesis of ethylal
Aldol condensation followed by dehydration		
acetone to diacetone alcohol (DAA) and mesityl	Anion exchange resin	High selectivity towards DAA; enhanced conversion

oxide		level
n-butaraldehyde to 2-ethyl hexenal	Aqueous alkaline solution	Formation of trimers/tetramers of aldehyde is avoided
Hydration/dehydration		
ethylene oxide + water = ethylene glycol	Cationic/anionic exchanger resins	To enhance selectivity towards MEG and avoid formation of diethylene glycol (DEG); attain better temperature control over the exothermic reaction
hydration of cyclohexane to cyclohexanol	SiO_2/Ga_2O_3	Surpass equilibrium conversion
Alkylation/trans-alkylation/dealkylation		
benzene + propylene = cumene	Union Carbide- LZY-82 molecular sieves	Use of exotherm of reaction; high purity cumene
isobutene + propylene/butylenes = highly branched paraffins	Lewis acid promoted inorganic oxide catalyst	Selectivity for C_7/C_8 branched alkanes
Isomerisation		
α–isophorone = β-isophorone	Adipic acid, ZSM-5,	To surpass the equilibrium conversion

	alumina	
n-paraffin to *iso*-paraffins	Chlorinated alumina catalyst, presence of hydrogen (< 8 bar)	To increase the octane value of paraffin stock
Chlorination		
dichlorobenzene to trichlorobenzene		To increase selectivity towards trichlorobenzene
dichlorodimethyl silane to dichloro (chloromethyl) silane	photochlorination	Increased yield towards monochlorinated product
Hydrogenation/hydrodesulfurization/ dehydrogenation		
hydrogenation of benzene to cyclohexane	Alumina supported Ni catalyst	Avoids formation of methyl cyclopentane and cracking products; used for removal of benzene from light reformate
hydrogenation of acytelene		For removal of butadiene from crude C_4 stream
Metathesis/disproportionation		
butene-1 = propylene + pentene or	Activated metal oxide	To surpass equilibrium limitation, increase in selectivity

butene-1 = ethylene + trans hexene-2		and operation under mild conditions
Condensation of aldehydes		
formaldehyde to trioxane	Strong acid catalyst hydrophobic shape selective (modified ZSM-5)	To enhance conversion
Dimerisation/Oligomerisation		
oligomerisation of C_4 iso-olefins	Solid phosphoric acid, cation exchange resins	To produce octane boosting oligomers; alternative to HF alkylation process
Carbonylation		
methanol/dimethyl ether + CO = acetic acid	Homogeneous system	Production of high purity acetic acid

(Source: Reactive distillation: status and future directions, Kai Sundmacher and Achim Kienle (*Eds*.))

Apart from functioning as a reactor and distillation, RD column can be an efficient separator to enhance the recovery rate and further purification of chemicals. Reactions such as esterification and acetalisation are suitable to be used in the RD column. Theoretically, the production of biodiesel through esterification using reactive distillation as proposed in this study can be fully-exploited. Furthermore, component to be removed is allowed to react in the distillation column and the resultant product can be separated simultaneously.

Reactive distillation (RD) has many distinctive advantages over sequential processing, such as fixed-bed reactor followed by a fractionating column, in which the distillate or bottom of the reaction mixture is recycled to the reactor inlet. The most crucial advantage in use of RD for equilibrium-controlled reactions is the elimination of conversion limitations by continuous removal of products from the reaction zone. Apart from increased conversion the following benefits can be obtained:

1. An important advantage of RD technology is a reduction in capital investment, because two process steps are able to be carried out in the same device. This integration leads to lower costs in pumps, piping and instrumentation.
2. If RD is applied to exothermic reaction, the reaction heat can be used for vaporisation of liquid and thus leads to saving of energy costs by the reduction of reboiler duties.
3. The maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture, so that the danger of hot spot formation on the catalyst is reduced significantly. A simple and reliable temperature control can be achieved.
4. Product selectivities can be improved due to a fast removal reactants or products from the reaction zone. By this, the probability of consecutive reactions, which may occur in the sequential operation mode, is lowered.
5. If the reaction zone in the RD-column is placed above the feed point, poisoning of the catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems.

When RD-technology is to be applied in industry scale, there are three constraints need to be fulfilled for harmonisation:

1. RD technology can be used only there is a possibility that the temperature window of the vapour-liquid equilibrium is equivalent to the reaction temperature. If the column operating pressure is to be changed, the temperature window will be altered as well. The thermal stability of the catalyst can limit the upper operation temperature of the distillation column.
2. Moreover, the necessity of wet pellets the chemical reaction has to occur entirely in the liquid phase.
3. It is extreme costly to change the catalyst in a structured catalytic packing catalysts with a long lifetime.

2.5.2 Reactive Distillation Process Development

As described earlier, reactive distillation (RD) may stand the chance in chemical industries in improving the structure of a process. By rule of thumb, the combination of distillation and reaction is plausible, only if the conditions of both operations are met and synchronised. Supporting argument claims that the reactions have to provide reasonable conversions in ascertain temperature and pressure levels which these data are comprehensively acceptable in a distillation column conditions.

Besides that knowing the important of the operating pressure and temperature in RD, catalyst types play a deeper measurement to understand RD column. The difference in using homogeneous and heterogeneous catalysts in the column also determine the cost of recycle back the catalyst. Homogeneous catalysts are widely used in most processes

however it is vitally need a separation step to recycle back the catalyst which increases the cost of recycling. It nonetheless can be avoided by using heterogeneous catalysts.

$$esterification: alcohol + acid \leftrightarrow ester + water \tag{2.1}$$

$$\frac{d[ester]}{dt} = k^{+}[alcohol][acid] - k^{-}[ester][water] \tag{2.2}$$

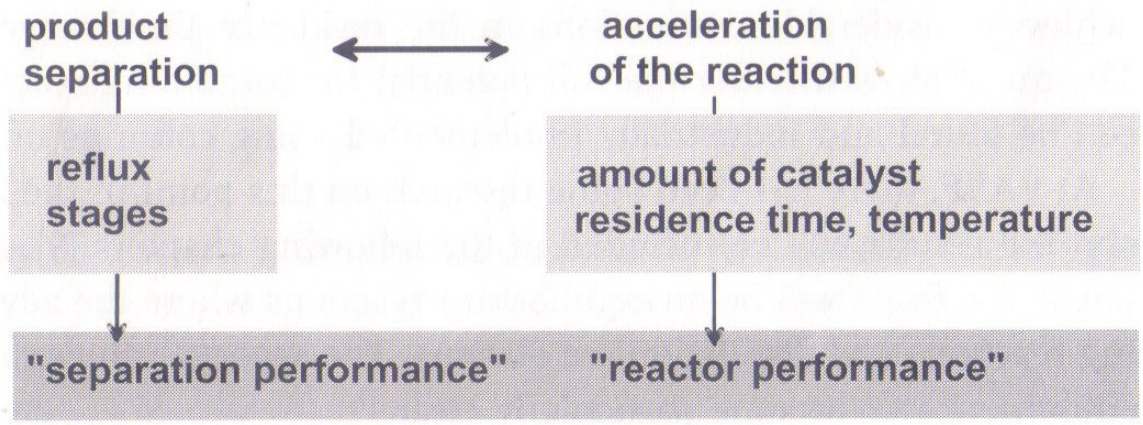

Figure 2.1 Interaction of reaction and separation.

From equation 2.1 and equation 2.2, it can be deduced that both equations will favour more products if the reaction is accelerated forward. According to Le Chatelier's principle, reactions can be influenced by temperature and amount of catalyst used. By increasing the temperature or the amount of catalyst, the forward reaction is accelerated by means of more removal of products in avoidance a change in concentrations in the production stream. The measurement of the product concentration (intensity of the product) and column efficiency are respectively termed as separation performance and reactor performance (Sundmacher and Kienle, 2003).

The maintainability of the reactive distillation column will be purely based on the separation performance but also the ratio of separation performance/reactor

performance in order to measure the extent of the main and secondary reactions proceed to a comparable of an industrial-scale reaction column. To achieve the construction by means of separating reaction and product separation, it can be done when the reaction is carried out in the presence of a heterogeneously catalysed at the downcoming stream or with side reactors at the column.

Besides that, the use of reactive distillation column is most effective to be considered in reactions that are extremely fast in achieving a significant conversion in the residence time range of such columns.

For a simple equilibrium reaction, the reaction equation can be described like this as shown in equation 2.3 below:

$$A_1 + A_2 \leftarrow \frac{k_1}{k_{min\ 1}} \rightarrow A_3 + A_4 \tag{2.3}$$

The rate constants for the forward and reverse reaction may be different from each other. Equation 2.3 shows a general reversible equation that applicable to certain chemical equilibrium. However, the equilibrium state (when the reaction velocity goes to zero) can be described using the law of mass action as shown in equation 2.4 below:

$$\frac{c_3^* c_4^*}{c_1^* c_2^*} = \frac{k_1}{k_{min\ 1}} = K_c \tag{2.4}$$

While the conversion of the stoichiometrically limiting reactant, for example component 1, in the equilibrium state is shown in equation 2.5 as below:

$$U_1^* = 1 - \frac{V c_3^* c_4^*}{V_0 c_1^* c_2^* K_c} \tag{2.5}$$

In reactive distillation column, there are two distinguishable operating parameters can be considered:

1. Range of conversion which is influenced mainly by the concentration of the product removed in the product stream, which is known as 'controlled by distillation'.
2. Range of conversion which is influenced mainly by the residence time and the reaction constant, which is known as 'controlled by kinetics'.

Reactions that take place inside a reactive distillation column can be divided into two consecutive reaction paces i.e. slow reaction and fast reaction. A reaction is considered slow when the reaction time is slow which correlate to the low residence time. A fast reaction does not require long residence time as the reaction is capable to reach equilibrium in the residence time range that is typical for column internals. Basically, relative volatility plays a role in determining the type of separation steps needed based on the reaction paces. This can be shown in Fig. 2.2 below:

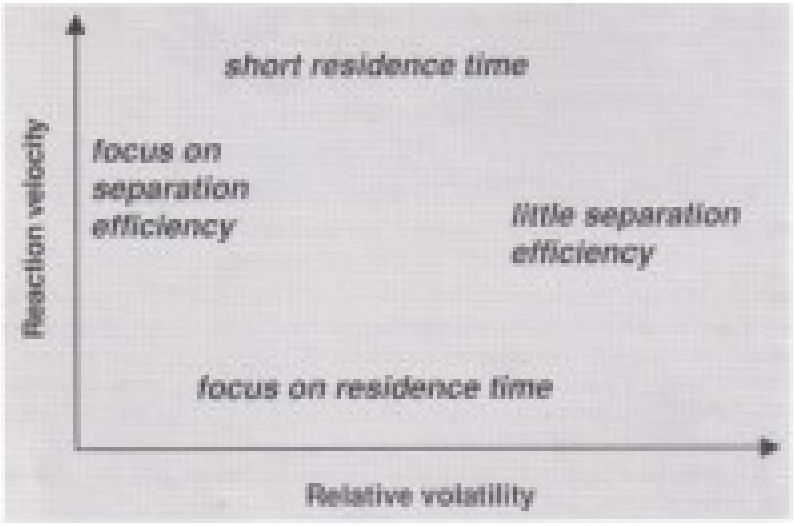

Figure 2.2 Design with respect to residence time and relative volatility.